

PATENT SPECIFICATION

Inventors: LOUIS ALOIS MIKESKA and DONALD FRED KOENECKE

812,526



Date of Application and filing Complete Specification: July 15, 1957.

No. 22331/57.

Complete Specification Published: April 29, 1959.

Index at acceptance:—Class 2(3), C2(A2:A13:R15:T15), C3A5(C1B1:C1B2:C1B3:C2:F3B), C3A10E4A5B, C3A10E5F(1A:2B:3C), C3A13A1(A2:F1).

International Classification:—C07c.

COMPLETE SPECIFICATION

Durene Dialdehyde and its preparation

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

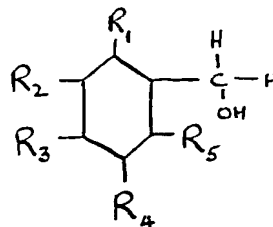
This invention relates to oxygen-containing aromatic compounds and to methods of synthesizing them. More particularly it relates to carbonyl compounds such as aldehydes and carboxylic acids obtainable by oxidation of aromatic alcohols such as benzyl alcohol, bis-hydroxymethyl benzene and the various higher homologues thereof. In its preferred embodiment the invention relates to tetramethyl terephthalyl dialdehyde and the preparation of this compound by oxidation of bis-hydroxymethyl durene.

Aromatic aldehydes and acids, and particularly the dibasic compounds of this sort, represent valuable chemicals which have many potential uses in the preparation of plastic, resinous or fiber-forming materials and as intermediates in various chemical syntheses such as the preparation of esters, amides, ethers and the like. However, as a rule, they are difficult to obtain.

It is the object of the present invention to provide new oxygen-containing aromatic compounds and to provide a new method for preparing monobasic or dibasic carbonyl compounds by oxidation of aryl carbinols or dicarbinols. Aromatic carbinols having a primary group are used and yield the corresponding aldehydes upon oxidation. One of the more specific objects is to provide an effective method for preparing oxygenated durene derivatives, notably tetramethyl terephthalyl dialdehyde.

The reagents used are hydroxymethyl
[Price 3s. 6d.]

aromatics, for example benzyl alcohol, o-, m-, and p-bis-hydroxymethyl benzene and nuclearly alkylated benzyl alcohols having 1 to 5 alkyl substituents of 1 to 20 carbon atoms, particularly para-bis-hydroxymethyl para-xylene, bis-hydroxymethyl durene and bis-hydroxymethyl isodurene. Naphthalene and anthracene derivatives, having 1 to 7 and 1 to 9 alkyl substituents, respectively, of 1 to 20 carbon atoms, and 1 or 2 hydroxymethyl substituents may also be used, for example, the alcohols produced by reacting alkyl substituted or chloromethyl naphthalene with aqueous alkali. The compounds used in the present invention can be represented by the formula



wherein one of said R_1 to R_5 radicals may be hydrogen, an alkyl radical of 1 to 20 carbon atoms or a hydroxymethyl radical; and the other four of said R_1 to R_5 radicals may be hydrogen or alkyl radicals of 1 to 20 carbon atoms.

Bis-hydroxymethyl durene is particularly preferred because its compact but fully substituted nature and the para position of its two hydroxymethyl groups result in the formation of compounds which are especially valuable in the preparation of linear fiber-forming polymers. Somewhat similar results can also be obtained with other cyclic compounds having two carbinol groups in the para position such as p-bis-hydroxymethyl benzene, 2,5-bis-hydroxymethyl toluene, 1,4-dimethyl-2,5-bis-

hydroxymethyl benzene, and so on. Furthermore, if the structure of the final product need not be linear, as in molding resins or insecticides, the two carbinol groups need not be in the para position with respect to each other. In such an event glycols derived from mixed xylenes or isodurene represent particularly useful raw materials.

Some of the foregoing cyclic alcohols are well known and others can be obtained from various sources. For instance, they can be obtained by conversion of the corresponding chloromethyl compound, which in turn can be advantageously prepared by the chloromethylation of an aromatic hydrocarbon with a chloromethyl alkyl ether in the presence of acetic anhydride. In converting the chloromethyl compound to the corresponding carbinol the former may be reacted, for example, with sodium acetate to form an ester and sodium chloride, and the ester can then be hydrolyzed in any convenient manner, e.g., by digestion with potassium hydroxide. One convenient method of making the hydroxymethyl compounds has been described, for example, by Rhoad and Flory, *Journal of the American Chemical Society*, 72, 2214 (1950).

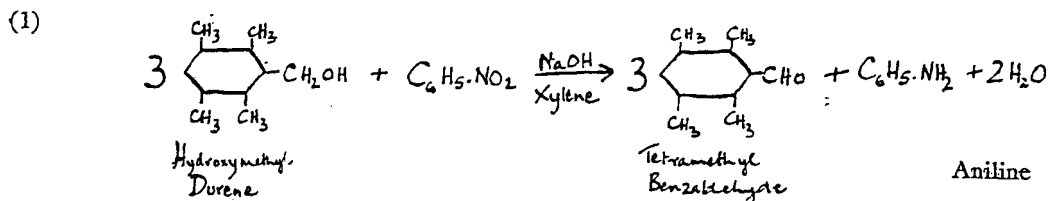
In the process of the present invention an aromatic carbinol or glycol is oxidized to the corresponding aldehyde, or dialdehyde with the aid of a nitrated aromatic compound, for example, a nitrobenzene, nitrotoluene, nitroxylenes or nitronaphthalene. Mononitrated aromatics such as nitrobenzene and nitrotoluene are preferred since the polynitro compounds tend to give more complex by-products

and some of them, of course, are rather highly explosive.

In preparing the aldehyde, the appropriate alcohol is refluxed with a molecular excess of mononitroaromatic, e.g., 1.1 to 2.0 moles of nitrobenzene per mole of alcohol in the presence of a small amount, e.g., 0.1 to 0.5 mole, of a base catalyst such as sodium or potassium hydroxide, and preferably about 2 to 4 volumes (per volume of reaction mixture) of an inert, water immiscible entraining agent having a boiling point between 50 and 150° C., for example, xylene, toluene, benzene or saturated naphtha. An increase in the amount of base catalyst increases the oxidation rate, but also promotes the formation of a carboxylic acid by-product at the expense of aldehyde formation. Unless such acid is particularly desired, the optimum amount of catalyst is, therefore, arrived at as a compromise between a suitable reaction rate and aldehyde yield.

As the reaction mixture is refluxed at temperatures which may range between about 100° and 300° C., water is liberated and driven off. Collection of this water in a water trap at temperatures which may range between about 15° and 25° C. can therefore serve as a convenient index of the progress of the reaction. A small amount of soap is formed by reaction of the alkali with the acid produced in the reaction. On completion of the latter the soap may be filtered off.

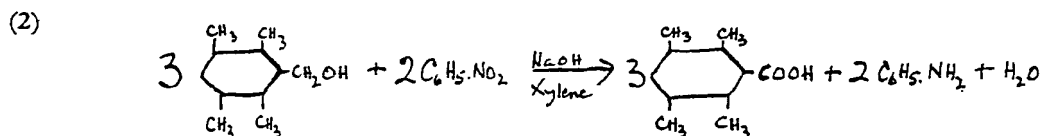
The main oxidation reaction of an aromatic carbinol in forming the corresponding aldehyde is illustrated by following equation (1):



As was indicated before, some of the alcohol is also converted to an acid, or rather a water-soluble alkali soap thereof, and some azo-

benzene is also formed.

The formation of an acid directly from the alcohol can be represented by equation (2):

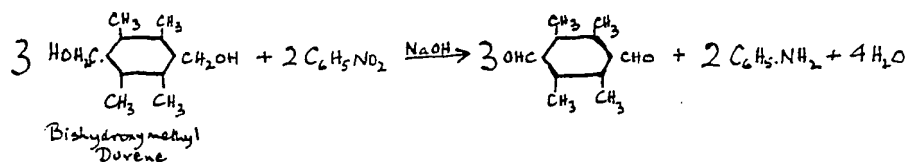


The isolation of the aldehyde from the organic phase of the reaction mixture, or of the acid which is normally present as a sodium soap in the aqueous phase, depends on the particular alcohol used. In some cases, as with benzyl alcohol, the aldehyde product can be recovered by distillation. In other cases, as with p-bis-(hydroxymethyl)durene, the aldehyde is conveniently recovered by fractional crystall-

ization. In still others, as with p-bis-(hydroxymethyl) benzene, it may be desirable to convert the aldehyde into an oxime or a hydrazone in order to facilitate the isolation. The aniline and azobenzene formed in the reaction can also be recovered and form valuable by-products.

Dialdehydes can be similarly prepared from glycols as shown in equation (3).

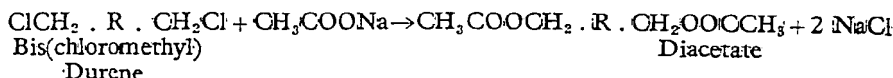
(3)



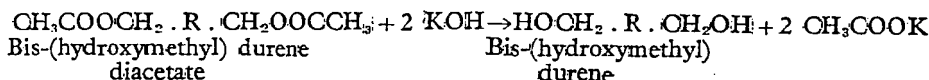
The invention will now be further illustrated by a specific example. Unless otherwise indicated it will be understood that all proportions and percentages of materials are expressed on a weight basis.

Preparation of Bis-(Hydroxymethyl)-Durene

A four-necked flask was equipped with a reflux condenser, a stirrer, a thermometer and a charging port. It was charged with 472 g. of bis-(chloromethyl) durene, 412 g. sodium



The 530 g. of diacetate prepared above were next charged into a reaction flask identical to that used before. 226 g. of KOH were dissolved in 2380 ml. of absolute ethanol, then the solution was added to the reaction flask. The use of absolute alcohol is desirable as otherwise the hydrolysis does not proceed with any degree of efficiency. The mixture was refluxed for two hours to hydrolyze the ester. The mixture was then poured into 5 liters of distilled water and acidified with hydrochloric acid. Since bis-(hydroxymethyl) durene is essentially insoluble in alcohol, the product was precipitated as hydrolyzed. The precipitated dicarbinol product was filtered and thoroughly washed until the wash water was no longer acid to litmus. The filtered and dried product



Preparation of 2,3,5,6-Tetramethyl Terephthalyl Dialdehyde

The dialdehyde was prepared from the dicarbinol by oxidation. For this purpose, in one synthesis, a three-necked flask was equipped with a reflux condenser and water trap, a stirrer and an addition port. The flask was charged with 200 g. of bis-(hydroxymethyl) durene (molecular weight 194), 200 g. of mononitrobenzene, 24 g. of pulverized technical grade sodium hydroxide and 600 cc. of xylene. The mixture was heated and refluxed at 145 to 148° C., and the water of reaction was trapped. After one and two hours, separate 12 g. portions of pulverized sodium hydroxide were added to speed up the oxidation.

After five hours of refluxing, 22 cc. of water had been collected, as against a theoretical amount of about 24 g. The reaction mixture was cooled to 85° C. and filtered. The

acetate and 2030 ml. of glacial acetic acid. The mixture was refluxed for 5 hours, then quenched with 2000 ml. of distilled water, filtered and washed thoroughly. The dry product, bis-(hydroxymethyl) durene diacetate, weighed 530 g., representing a 94% yield based on the theoretical. It was a white crystalline solid with a melting point of 181° C.

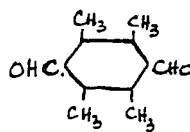
The preparation of the diacetate can be summarized by the following equation:

weighed 322 g., representing a 90% yield based on the theoretical input of 530 g. of diacetate.

The crude bis(hydroxymethyl) durene had a melting range of 235—245° C. in a capillary tube. Recrystallization from hot dioxane or dimethyl formamide brought the melting point to 245—247° C. Bis-(hydroxymethyl) durene, also referred to as 2,3,5,6-tetramethyl phenylene-1,4-dicarbinol, is a white crystalline solid not readily soluble in ether, hydrocarbons, chlorinated hydrocarbons or ketones. It can be dissolved in hot dioxane or dimethyl formamide.

The preparation of the dicarbinol can be summarized by the following equation:

insoluble fraction was found to contain 71 g. of unreacted bis-(hydroxymethyl) durene, and 7.0 g. of tarry acids. The filtrate was cooled and concentrated with successive crystallizations, yielding 83.8 g. of tetramethyl terephthalyl dialdehyde:



Steam distillation was then used to decrease the amounts of nitrobenzene, azobenzene and aniline in the mixture, and another subsequent crystallization yielded 15 g. more of the desired dialdehyde. Azobenzene and aniline were isolated as the by-products formed by the reduction of the nitrobenzene.

The final results were a 64.5% conversion of the bis-(hydroxymethyl) durene. Based on the isolated products, the selectivity to the dialdehyde was about 85%. The product, purified by repeated recrystallizations, had a melting point of 165° C.

In another synthesis the dialdehyde was prepared under somewhat different conditions. Using the same apparatus as just described, 200 g. of bis-(hydroxymethyl) durene were reacted with 150 g. of mononitrobenzene (a 77% excess) in the presence of 24 g. of pulverized technical sodium hydroxide using 600 cc. of toluene as the solvent and entraining agent for the water of reaction. A further difference was that the bis-(hydroxymethyl) durene was washed with dilute sodium hydroxide and dried before using.

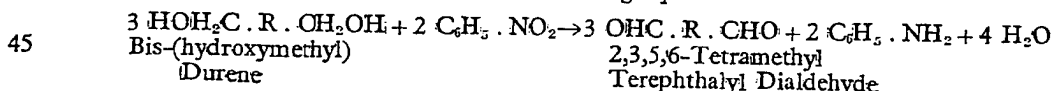
The mixture was heated and refluxed at 115—116° C. In two hours 32 cc. of water were collected and in 6.5 hours 51 cc. This is considerably in excess of the theoretical and

was attributed to insufficient drying of the washed bis-(hydroxymethyl) durene.

The reaction mixture was cooled and filtered at 90° C. The insoluble material contained 22.2 g. of unreacted bis-(hydroxymethyl) durene and 25 g. of tarry acids. Successive crystallizations of the filtrate at 15° C., -15° C., and -25° C. gave a yield of 114.5 g. of tetramethyl terephthalyl dialdehyde melting from 158—162° C. Additional dialdehyde product remained dissolved in the residual liquor together with benzene, azobenzene and aniline, but no further effort was made to recover it. Parenthetically it may be noted that the dialdehyde is very soluble in aniline.

The results of this oxidation indicated about 89% conversion of the bis-(hydroxymethyl) durene, with a selectivity of 82% to the tetramethyl terephthalyl dialdehyde based on the isolated oxidation products.

The main reaction is indicated by the following equation:

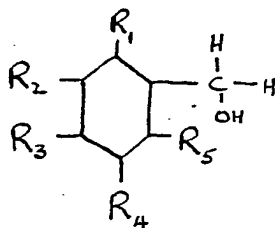


Similar results can be obtained when the invention is used, for instance, for making terephthalyl aldehyde by oxidation of bis-hydroxymethyl benzene, 2,5-dimethyl, terephthalyl dialdehyde by oxidation of 2,5-dimethyl-p-xylene, p-methyl benzaldehyde from p-hydroxymethyl toluene and so forth.

The dialdehydes may be used as intermediates in the preparation of polyacetals, suitable for the preparation of synthetic fibers. Alternatively, the dialdehydes may be further oxidized to give the corresponding diacids, which in turn may be used to make resinous or fiber-forming polyesters. The monobasic aldehydes may similarly be oxidized to the corresponding acids and esters which in turn can be used as synthetic lubricants, lubricating oil addition agents, plasticizers, insect repellants and the like.

WHAT WE CLAIM IS:—

1. A process for oxidizing an aromatic carbinol having the formula



wherein one of said R_1 to R_5 radicals may be hydrogen, an alkyl radical of 1 to 20 carbon atoms or a hydroxymethyl radical, and the other four of said R_1 to R_5 radicals may be hydrogen or alkyl radicals of 1 to 20 carbon

atoms, which comprises mixing said carbinol with a molal excess of a nitroaromatic compound, heating the mixture to oxidation temperature, and separating an aldehyde product from the mixture.

2. A process according to claim 1 wherein the aromatic carbinol is a dicarbinol having the formula $\text{HOH}_2 \cdot \text{C} \cdot \text{R} \cdot \text{CH}_2\text{OH}$ wherein R may be phenylene or an alkyl substituted phenylene radical.

3. A process according to claim 2 wherein said dicarbinol is 2,3,5,6-tetramethyl phenylene 1,4-dicarbinol.

4. A modification of the process as claimed in any one of claims 1 to 3 wherein the aromatic carbinol is a naphthalene or anthracene derivative having 1 to 7 and 1 to 9 alkyl substituents, respectively of 1 to 20 carbon atoms, and 1 or 2 hydroxymethyl substituents.

5. A process as claimed in any one of claims 1 to 4 wherein the carbinol is mixed with 1.1 to 2 mole equivalents of mononitro benzene, 0.1 to 0.5 mole equivalents of an alkali metal hydroxide and 2 to 4 volumes per volume of reaction mixture of a water-immiscible inert entraining agent having a boiling point between 50 and 150° C., the mixture heated to vaporize the entrainer and an aromatic aldehyde or ketone separated from the mixture.

6. A process according to claim 5 wherein the entrainer is a benzene hydrocarbon having 1 to 2 methyl substituents and wherein the reaction mixture is heated at reflux temperature.

7. 2,3,5,6 - Tetramethyl Terephthalyl dialdehyde.

8. A process for preparing aromatic aldehydes substantially as hereinbefore described in the examples.

K. J. VERYARD,
33, Davies Street, London, W.1,
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1959.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.